

Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate using GLC

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ABSTRACT

Activity coefficients at infinite dilution, γ_{13}^{∞} , for 32 organic compounds: alkanes, alk-1-enes, alk-1-yne, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, *tert*-butyl methyl ether and water in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPYR][CF₃SO₃] were determined by gas–liquid chromatography at the temperatures ranging from 298.15 to 368.15 K. The partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The selectivities for the *n*-hexane/benzene, cyclohexane/benzene, *n*-hexane/thiophene, cyclohexane/thiophene, benzene/thiophene and hexen-1-ene/*n*-hexane separation problems were calculated from the γ_{13}^{∞} and compared to the literature values for other ionic liquids, NMP and sulfolane.

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1. Introduction

This work is a continuation of our investigation into the determination of activity coefficients at infinite dilution, γ_{13}^{∞} , for different solutes in an ionic liquid using gas–liquid chromatography.

Our most important studies, recently published include measurements of γ_{13}^{∞} for organic solutes in the ionic liquids (ILs) based on the methylimidazolium cation: 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] [1], 1-ethyl-3-methylimidazolium trifluoroacetate [EMIM][TFA] [2], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF₃SO₃] [3] and 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN] [4]. Interesting results were published for the pyridinium-based ILs—the γ_{13}^{∞} were measured for 4-methyl-*N*-butylpyridinium tetrafluoroborate [5,6]. Only two references were found on γ_{13}^{∞} for pyrrolidinium-based ionic liquids, namely 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMPYR][NTf₂] [7,8]. The values of both activity coefficients and partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E,\infty}$, were almost the same for the imidazolium-based ILs with different alkane chains (methyl, ethyl, butyl, hexyl, octyl) and the same anion [NTf₂][−] [7]. However, the influence of the alkane chain at the imidazolium-based ILs, or the pyrrolidinium-based ILs was observed to be very similar [7,8].

Generally, lengthening the alkane chain on the imidazolium, or pyrrolidinium cation (for the ILs with the same [NTf₂][−] anion) causes a decrease in both the density of the IL, as well as γ_{13}^{∞} of the same solute (i.e. pentane, pent-1-ene, cyclohexane) in the IL at the same temperature [7,8]. On the other hand, increasing the alkyl chain length on the imidazolium cation results in a decrease of the upper critical solution temperature of the binary system (increasing solubility) of the liquid–liquid phase equilibria [9,10]. Also the selectivity for the separation of aromatic hydrocarbons/aliphatic hydrocarbons decreases with increasing length of the alkyl chain on the imidazolium cation of the IL [1–4].

In order to expand our knowledge about the nature of ILs, the influence of the anion on the thermodynamic properties of the pyrrolidinium-based ionic liquid with trifluoromethanesulfonate [CF₃SO₃][−] anion was studied in this work. The effect of anion {[CF₃SO₃][−] versus [NTf₂][−]}, and the effect of cation {[BMPYR]⁺ versus [BMIM]⁺} on the γ_{13}^{∞} , $\Delta H_1^{E,\infty}$ and the separation of aliphatic from aromatic hydrocarbons by extraction will be discussed. This paper presents γ_{13}^{∞} values for 32 solutes {alkanes, cycloalkanes, alk-1-enes, alk-1-yne, benzene, alkylbenzenes, alcohols, tetrahydrofuran (THF), thiophene, *tert*-butyl methyl ether (MTBE), and water} in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPYR][CF₃SO₃] at eight temperatures $T=298.15, 308.15, 318.15, 328.15, 338.15, 348.15, 358.15$ and 368.15 K.

Since the ILs have a negligible vapour pressure, gas–liquid chromatography, GLC, is a suitable method for measuring the activity coefficients at infinite dilution, γ_{13}^{∞} .

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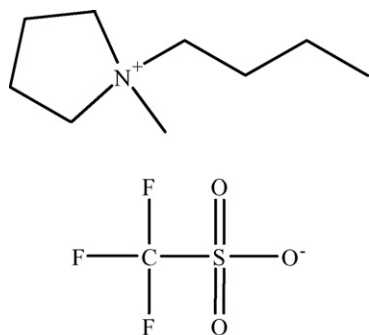
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2. Experimental

2.1. Materials or chemicals

The ionic liquid [BMPYR][CF₃SO₃] had a purity of >0.99 mass fraction and was supplied by Merck. The ionic liquid was further purified by subjecting the liquid to a very low pressure of about 5×10^{-3} Pa at a temperature of about 360 K for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The solutes, purchased from Aldrich and Fluka, had a purity above 0.99 mass fractions and were used without further purification because the GLC technique separated any impurities on the column. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by SUPELCO. This material was also purified by the same method used for the ionic liquid. The mass of the IL and Chromosorb was checked before conditioning and after loading. The same masses obtained before and after loading confirm that the IL and Chromosorb are clean, without water and volatile chemicals.

The structure of the investigated IL is presented below:



2.2. Experimental procedure

The experiments were performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software.

The column preparation and the packing method used in this work, has been described previously [1–4,11,12]. Glass columns of length 1 m and 4 mm internal diameter were used. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb into a solution of the ionic liquid in methanol followed by evaporation of the solvent using a rotary evaporator. The masses of the stationary phase and of the solid support were weighed with a precision ± 0.0001 g. The solvent column packing varied from 0.466 to 0.524 mass fraction of the ionic liquid, large enough to prevent any residual adsorption of solute onto the column packing, as was observed in recently published works [13,14]. For each temperature, the measurements were repeated by using two different columns with different mass percent packing. Care was taken to ensure that the methanol had completely evaporated from the IL coated solid before making up the column. Before experiments each column was conditioned by passing carrier gas at high flow rate (about $2 \text{ cm}^3 \text{ s}^{-1}$) and at the high temperature (about 360 K) over a period of about 8 h.

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) varied between 40 and 80 kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a pressure transducer implemented in the GC with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.1 hPa.

The carrier gas was helium and the flow rate of the carrier gas was determined using a calibrated soap bubble flowmeter which

was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any γ_{13}^∞ determinations were made. The flow rates were corrected for water vapour pressure and ranged from 1.1 to $2.5 \text{ cm}^3 \text{ s}^{-1}$. Solute injections ranged from 0.01 to $0.3 \mu\text{l}$ and were considered to be at infinite dilution on the column. Injection was provided manually with the syringe $1 \mu\text{l}$.

Experiments were carried out at different temperatures (in steps of 10 K) in the range from $T = 298.15$ to $T = 368.15$ K. The temperature of the column was maintained constant to within ± 0.02 K. The temperature of the column was controlled many times in the ovens of GC with an additional electronic thermometer P 550 (Dostmann Electronic GmbH). At a given temperature, each experiment was repeated 2–4 times to check the reproducibility. Retention times were generally reproducible within 0.001–0.01 min. At each temperature values of the dead time t_G identical to the retention time of a non-retainable component were measured. While our GC was equipped with a TCD detector, air was used as a non-retainable component. The estimated overall error in γ_{13}^∞ was less than 3%, taking into account the possible errors in determining the column loading, the retention times and solute vapour pressure. The GLC technique was tested for the system hexane in hexadecane at $T = 298.15$ K and the results compared very favourably with the literature values [15].

3. Theoretical basis

The equation developed by Everett [16] and Cruickshank et al. [17] was used in this work to calculate the γ_{13}^∞ of solutes in the ionic liquid.

$$\ln \gamma_{13}^\infty = \ln \left(\frac{n_3 RT}{V_N P_1^*} \right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \frac{P_o J_2^3 (2 B_{12} - V_1^\infty)}{RT} \quad (1)$$

In this work, subscript 1 refers to a solute, 2 refers to the carrier gas, and 3 refers to the solvent [BMPYR][CF₃SO₃]. n_3 is the number of moles of solvent on the column packing, R is a gas constant, T the column temperature, V_N denotes the net retention volume of the solute, P_1^* the saturated vapour pressure of the solute at temperature T , B_{11} the second virial coefficient of pure solute, V_1^* the molar volume of the solute, P_o the outlet pressure, $P_o J_2^3$ the mean column pressure, B_{12} (where 2 refers to helium), the mixed second virial coefficient of the solute and the carrier gas and V_1^∞ the partial molar volume of the solute at infinite dilution in the solvent. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation [18]:

$$\frac{B}{V_c} = 0.430 - 0.886 \left(\frac{T_c}{T} \right) - 0.694 \left(\frac{T_c}{T} \right)^2 - 0.0375(n-1) \left(\frac{T_c}{T} \right)^{4.5} \quad (2)$$

where n refers to the number of carbon atoms. Using the Hudson and McCoubrey combining rules [19,20], V_{12}^c and T_{12}^c were calculated from the critical properties of the pure components.

The pressure correction term J_2^3 is given by

$$J_2^3 = \frac{2 (P_i/P_o)^3 - 1}{3 (P_i/P_o)^2 - 1} \quad (3)$$

The net retention volume of the solute V_N , is given by

$$V_N = J_2^3 U_o (t_R - t_G) \quad (4)$$

where t_R and t_G are the retention times for the solute and an unretained gas, respectively, U_o is the column outlet flow rate.

The vapour pressure values were calculated using equation and constants taken from the literature [21–23]. Critical data used to calculate B_{11} and B_{12} , and ionization energies used in the calculation of T_{12}^c , were obtained from the literature [24,25].

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